PATENT

Attorney Docket No. 03848.04649

PROVISIONAL PATENT APPLICATION

COMPOSITIONS AND METHODS INVOLVING DIRECT WRITE OPTICAL LITHOGRAPHY

Inventor(s):

CALVIN F. QUATE, a citizen of the United States of America residing in Stanford, California and DAVID STERN, a citizen of the United States of America, residing in Mountain View, California.

COMPOSITIONS AND METHODS INVOLVING DIRECT WRITE OPTICAL LITHOGRAPHY

Background of the Invention

Polymer arrays, such as the GeneChip® probe array (Affymetrix, Inc., Santa Clara, CA), can be synthesized using light-directed methods described, for example, in U.S. Patent Nos. 5,143,854; 5,424,186; 5,510,270; and PCT published application no. WO 95/11995. Light-directed methods often involve the use of masks that permit the light used for synthesis to reach certain regions but not others. See, for example, U.S. Patent Nos. 5,593,839 and 5,571,639. The photochemical steps in the synthesis of nucleic acid arrays, for example, are often performed by contact printing or proximity printing. A chrome-on-glass mask is placed in contact with the wafer, or nearly in contact, and the wafer is illuminated through the mask by light having an appropriate wavelength. Masks can be costly and are capable of being damaged or lost. A photolithographic method that does not require chrome-on-glass masks obviates such difficulties and is otherwise generally useful.

Summary of the Invention

The present invention involves polymer array synthesis with a maskless system: a Direct Write System where the patterns of illumination are stored in a computer. In the Direct Write

System each cell or pixel, is illuminated with an optical beam of suitable intensity and the printing of an individual cell is determined by computer control. Synthesis is accomplished using a class of devices known as spatial light modulators. A spatial light modulator is a device in which a controlling (write) high beam modulates the amplitude or phase of a readout light beam. As used herein, a spatial modulator means a reconfigurable device for transmitting, reflecting or changing the polarization of a light beam.

The present invention also provides polymer arrays synthesized during the methods taught herein.

Brief Description of the Drawings

Figure 1 shows one embodiment of the invention.

Figure 2 is a diagrammatic representation of an alternate embodiment of the invention employing a microlens array. DMD™ stands for Digital Micromirror Device (Texas Instruments, Inc., Dallas, TX, USA). GLV™ stands for Grating Light Valve (Silicon LightMachines, Sunnyvale, CA, USA).

Figure 3 illustrates a MicroLens array in the form of Fresnel Zone Plates.

Detailed Description of the Invention

Certain embodiments of the invention involve the use of micromachined mechanical modulators to direct the light to predetermined regions of the substrate on which the polymers are being synthesized. Such predetermined regions are discussed herein as cells or pixels. The mechanical modulators come in at least two types.

One type of mechanical modulator uses small metal mirrors to deflect the light beam on and off the individual cells. An example is the programmable micro-mirror array manufactured by Texas Instruments, Inc., Dallas, Texas, USA. The Texas Instruments' array consists of 640 x 480 mirrors (the VGA version) or 800 x 600 mirrors (the super VGA version). Devices with more mirrors are under development. Each mirror is 16 μm x 16 μm and there are 1-μm gaps between mirrors. The array is designed to be illuminated 20 degrees off axis. Each mirror can be turned on (tilted 10 degrees in one direction) or off (tilted 10 degrees in the other direction). A lens (on axis) images the array onto a target. When a micro-mirror is turned on, light reflected by the micro-mirror passes through the lens and the image of the micro-mirror appears bright. When a micro-mirror is turned off, light reflected by the micro-mirror misses the lens and the image of the micro-mirror appears dark. The array can be reconfigured by software (i.e., every micro-mirror in the array can be turned on or off as desired) in a fraction of a second. Texas Instruments markets the arrays primarily for projection display applications (e.g., big-screen video) in which a highly magnified image of the array is projected onto a wall or screen. The present invention shows, however, that which appropriate optics and an appropriate light source, a programmable micro-mirror array can be used for photolithographic synthesis, and in particular for polymer array synthesis.

A second mechanical modulator, such as that available from Silicon LightMachines, relies on micromachined pixels that can be programmed to either reflective or diffractive (Grating Light Valve™ technology). Information regarding certain of the mechanical modulators discussed herein is obtained at http://www.ti.com (Texas instruments) and http://siliconlight.com. (Silicon LightMachines).

A preferred embodiment of synthesizing polymer arrays with a programmable micro-mirror array takes place as follows:

1. A computer file is generated. This file specifies, for each photolithography step, which mirrors in the array need to be on and which need to be off.

2. The chip or wafer containing many chips is coated with photoresist on the synthesis surface, is mounted in a holder on the photolithography apparatus so that the synthesis surface is in the plane where the image of the micro-mirror array will be formed. If the features to be synthesized are large, mounting might be sufficiently reproducible that no alignment or focusing is necessary. Otherwise, means for aligning and focusing the chip or wafer is provided.

3. The micro-mirror array is programmed for the appropriate configuration.

4. The shutter in front of the arc lamp is opened, the chip or wafer is illuminated for the desired amount of time, and the shutter is closed.

5. If a wafer is being synthesized, a stepping-motor-driven translation stage moves the wafer by a distance equal to the desired center-to-center distance between chips.

6. Steps 4 and 5 are repeated until each chip in the wafer has been exposed.

7. The necessary wet chemical steps take place. If doing front-side synthesis, the chip or wafer must be removed from the photolithography apparatus and mounted on a wet chemistry flow cell. If doing backside synthesis, the chip or wafer mount on the photolithography apparatus can be the wet chemistry flow cell; in this case the chip or wafer does not have to be removed and remounted. For this reason, backside synthesis is preferred. Contact or proximity printing requires frontside synthesis for high resolution. Fortunately, projection photolithography does not.

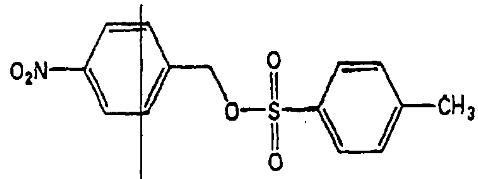
8. The chip or wafer is recoated with photoresist. This is often done by spin coating (and therefore the chip or wafer must be removed from the flow cell). Means of applying the photoresist that does not require removal of the chip or wafer from the flow cell can also be used. An example of an alternative to spin coating is the incorporation of the photoresist into a gel that fills the flow cell.

9. Steps 2-8 are repeated until the synthesis is complete.

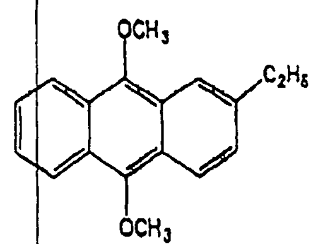
Substrates coated with photoresist are employed in preferred embodiments of the invention. The use of photoresist with photolithographic methods for fabricating polymer arrays is discussed in McGall et al., *Chemtech*, pp. 22-32 (February 1997); McGall et al., *Proc. Natl. Acad. Sci., U.S.A.*, Vol. 93, pp. 13555-13560 (Nov. 1996). The use of photoacid generators is taught in U.S. Provisional Application No. 60/030,826, filed November 14, 1996. These methods are particularly useful in the present invention.

When synthesizing nucleic acid arrays, the photochemical processes used to fabricate the arrays is preferably active at or above 365 nm to avoid photochemical degradation of the polynucleotides. Many photoacid generators (PAGs) based on *o*-nitrobenzyl chemistry are useful at 365 nm. When using the mirror array from Texas Instruments, the PAG is preferably sensitive above 400 nm to avoid damage to the mirror array. To achieve this, *p*-nitrobenzyl esters can be used in conjunction with a photosensitizer. For example, *p*-nitrobenzyltosylate and 2-ethyl-9,10-dimethoxy-anthracene can be used to photochemically generate toluenesulfonic acid at 405 nm. See S.C. Busman and J.E. Trend, *J. Imag. Technol.*, 1985, **11**, 191; A. Nishida, T. Hamada, and O. Yonemitsu, *J. Org. Chem.*, 1988, 53, 3386. In this system, this sensitizer absorbs the light and then transfers the energy to the *p*-nitrobenzyltosylate, causing dissociation and the subsequent

release of toluensulfonic acid. Alternate sensitizers, such as pyrene, *N,N*-dimethylnapthylamine, perylene, phenothiazine, canthone, thiocanthone, actophenone, and benzophenone that absorb light at other wavelengths are also useful. A variety of photoresists sensitive to 436-nm light are available.



***p*-nitrobenzyltosylate**



2-ethyl-9,10-dimethoxynapthylene

Although preferred spatial light modulators include those available from Texas Instruments and Silicon LightMachines, various types of spatial light modulators exist and are usable in the practice of the present invention. See *Electronic Engineers' Handbook*, 3rd Ed., Fink, D.G. and Christiansen, D. Eds., McGraw-Hill Book Co., New York (1989). Deformable membrane mirror arrays are available from Optron Systems Inc. (Bedford, MA). Liquid-crystal spatial light modulators are available from Hamamatsu (Bridgewater, NJ). Spatialight (Novato,

CA), and other companies. Liquid-crystal displays (e.g., in calculators and notebook computers) are also spatial light modulators useful for photolithography particularly to synthesize large features. To synthesize smaller features, reduction optics are required.

Other light modulators are useful in the present invention. Deformable membrane mirror arrays are available from Optron Systems Inc. (Bedford, MA). Liquid-crystal spatial light modulators are available from Hamamatsu, Spatialight (Novato, CA). Liquid-crystal displays (e.g., in calculators and notebook computers) are spatial light modulators are useful with reduction optics or only synthesize large features. Some spatial light modulators may be better suited than the Texas Instruments device for use with ultraviolet light and would therefore be compatible with a wider range of photoresist chemistries. One skilled in the art will choose the spatial modulator that is compatible with the chosen wavelength of illumination and synthesis chemistries employed. For example, the device from Texas Instruments (DMD™) should not be used with ultraviolet illumination.

Some spatial light modulators are designed to modulate transmitted rather than reflected light. A transmissive spatial light modulator can have certain advantages. Reflective spatial light modulators require a large working distance between the modulator and the lens so that the lens does not block the incident light. Designing a high performance lens with a large working distance is more difficult than designing a lens of equivalent performance with no constraints on the working distance. With a transmissive modulator the working distance does not have to be long and lens design is therefore easier. Some transmissive spatial light modulators might be useful for proximity or contact printing (i.e., with no lens at all, just the modulator very close to the chip or wafers).

Although discussed herein in reference to polymer array synthesis, one skilled in the art will appreciate that the present invention has a variety of applications including without limitation silicon micromachining and custom semiconductor chip manufacturing.

One skilled in the art will choose a spatial modulator that is compatible with the chosen wavelength of illumination and synthesis chemistries employed. For example, Texas Instruments' micro-mirror array is not compatible with ultraviolet illumination.

Patents and/or applications related to the present invention include U.S. Patent No. 5,384,261 (issued January 24, 1995), 5,677,195 (issued November 14, 1997) and application Serial No. 08/426,202 (filed April 21, 1995), all of which are hereby incorporated by reference for all they teach and disclose.

<u>Example</u>

A Texas Instruments "SVGA DLP™" subsystem with optics is used. In addition to the micro-mirror array, it includes a light source, a color filter wheel, a projection lens, and electronics for driving the array and interfacing to a computer. The filter wheel is replaced with a 400-410 nm bandpass filter. For additional brightness at 400-410 nm, the light source can be replaced with an arc lamp and appropriate homogenizing and collimating optics. The lens included with the device is intended for use at very large conjugate ratios. Therefore, it is replaced with an appropriate lens or set of lenses.

A symmetric lens system used at 1:1 magnification is desirable because certain aberrations (distortion, lateral color, coma) are zero by symmetry, and lens design is simplified because there are only half as many variables as in an asymmetric system having the same number of surfaces.

However, at 1:1 magnification the maximum possible chip size is 10.88 mm 8.16 mm with the VGA device, or 13.6 mm with the super VGA device. Synthesis of 12.8 mm x 12.8 mm chips uses an asymmetric optical system (e.g., a magnification of about 1.25:1 with SVGA device) or a larger micro-mirror array (e.g., 1028 x 768 mirrors) if the mirror size is constant.

In certain applications, a relatively simple lens system, such as a back-to-back pair of achromats or camera lens, is adequate. A particularly useful lens for some applications is the Rodenstock (Rockford, IL) Apo-Rodagon D. This lens is optimized for 1:1 imaging and gives good performance at magnifications up to about 1.3:1. Similar lenses may be available from other manufacturers. With such lenses, either the Airy disk diameter or the blur circle diameter will be rather large (maybe 10 um or larger). See *Modern Optical Engineering*, 2d Edition, Smith, W.J., ed., McGraw-Hill, Inc., New York (1990). For higher-quality synthesis, the feature size is several times larger than the Airy disk or blur circle. A custom-made lens with resolution of about 1-2 um over a 12.8 mm x 12.8 mm field is particularly desirable.

One embodiment that is particularly useful when extremely high resolution is required involves imaging the micromirror array using a system of the type shown in Fig. 2. In this system, a lens images the micromirror array onto an array of light concentrators. The array of light concentrators includes both imaging and non-imaging concentrators. Each element of the microlens array then focuses light onto the chip or wafer. For example, if an SVGA DLP device is imaged with 1:1 magnification onto a microlens array, an appropriate microlens array can consist of 800 x 600 lenses with 17 μm center-to-center spacing. Alternatively, the microlens array can consist of 400 x 300 17 μm diameter lenses with 34 μm center-to-center spacing, and with opaque material (e.g., chrome) between microlenses. An advantage of this alternative is that

cross-talk between pixels is reduced. The light incident upon which each microlens can be focused to a spot size of 1-2 μm. Because the spot size is much less than the spacing between microlenses, a 2-axis translation stage (having, in these examples, a range of travel of at least either 17 μm x 17 μm or 34 μm x 34 μm) is necessary if complete coverage of the chip or wafer is desired.

Imaging concentrator microlenses can be diffractive or refractive. Refractive microlenses can be conventional or gradient-index. An example of a diffractive microlens array is shown in Figure 3. Alternatively an array of non-imaging light concentrators can be employed. An example of such an approach would include a short piece of optical fiber tapered to a tip having a submicron diameter.

Although discussed herein in reference to polymer array synthesis, one skilled in the art will appreciate that the present invention has a variety of applications including without limitation silicon micromachining and custom semiconductor chip manufacturing. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entirety for all purposes.

WHAT IS CLAIMED IS:

1. A method for deprotecting reaction sites on a substrate comprising:

providing a substrate having protected reaction sites;

providing a light source and a spatial light modulator, wherein said spatial light modulator modulates intensity; and

directing light from said light source to said spatial modulator wherein said light emerging from said spatial modulator deprotects said protected reaction sites.

2. A method of deprotecting reaction sites on a substrate comprising:

providing a substrate having protected reaction sites, a light source, an intensity modulating spatial light modulator, and a lens;

orienting said substrate, light source, spatial light modulator, and lens such that when said light source illuminates, illumination from said light source is modulated by said spatial light modulator and imaged at said substrate by said lens; and

illuminating said substrate, whereby said imaging at said substrate deprotects said protecting reaction regions.

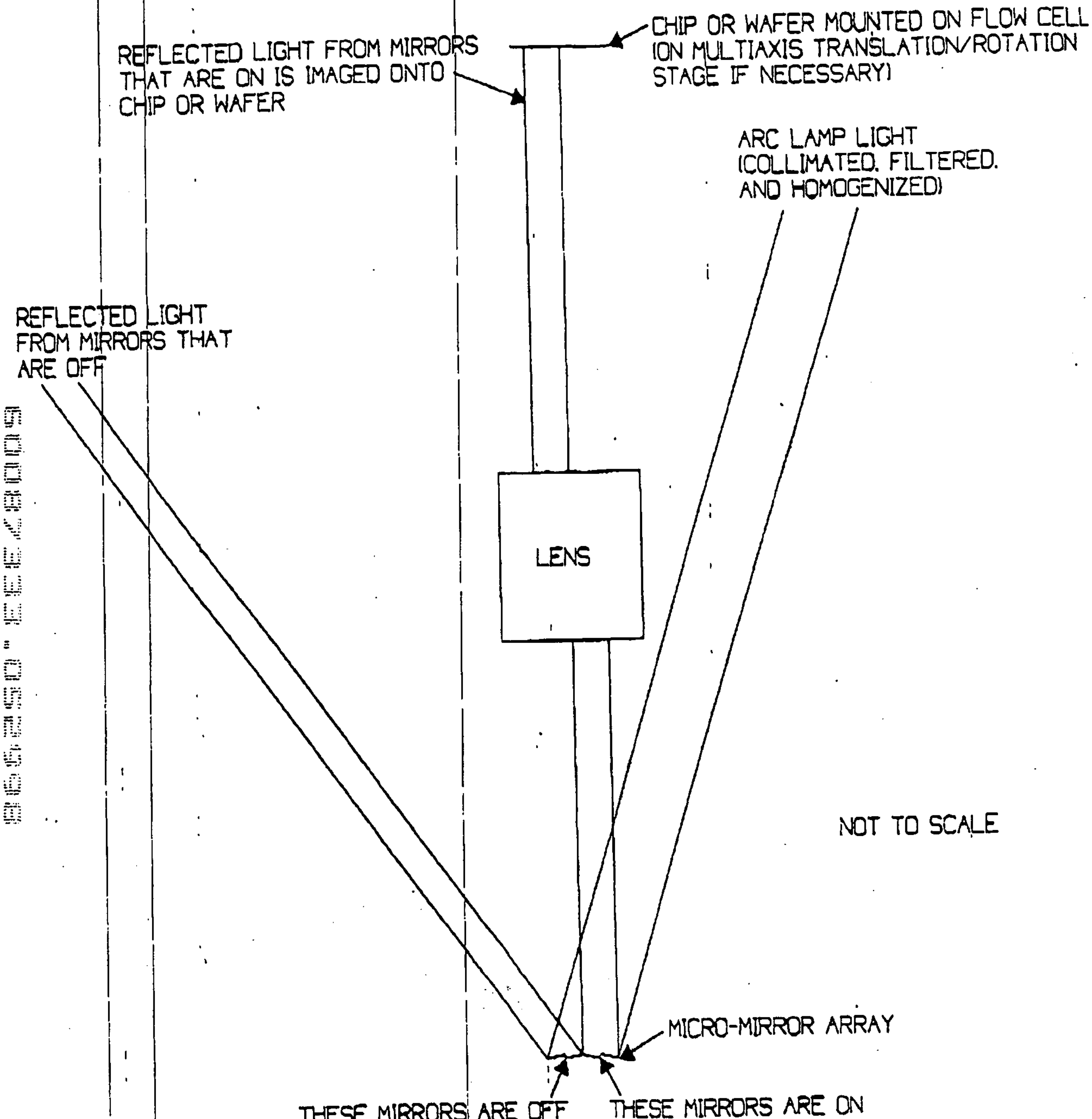
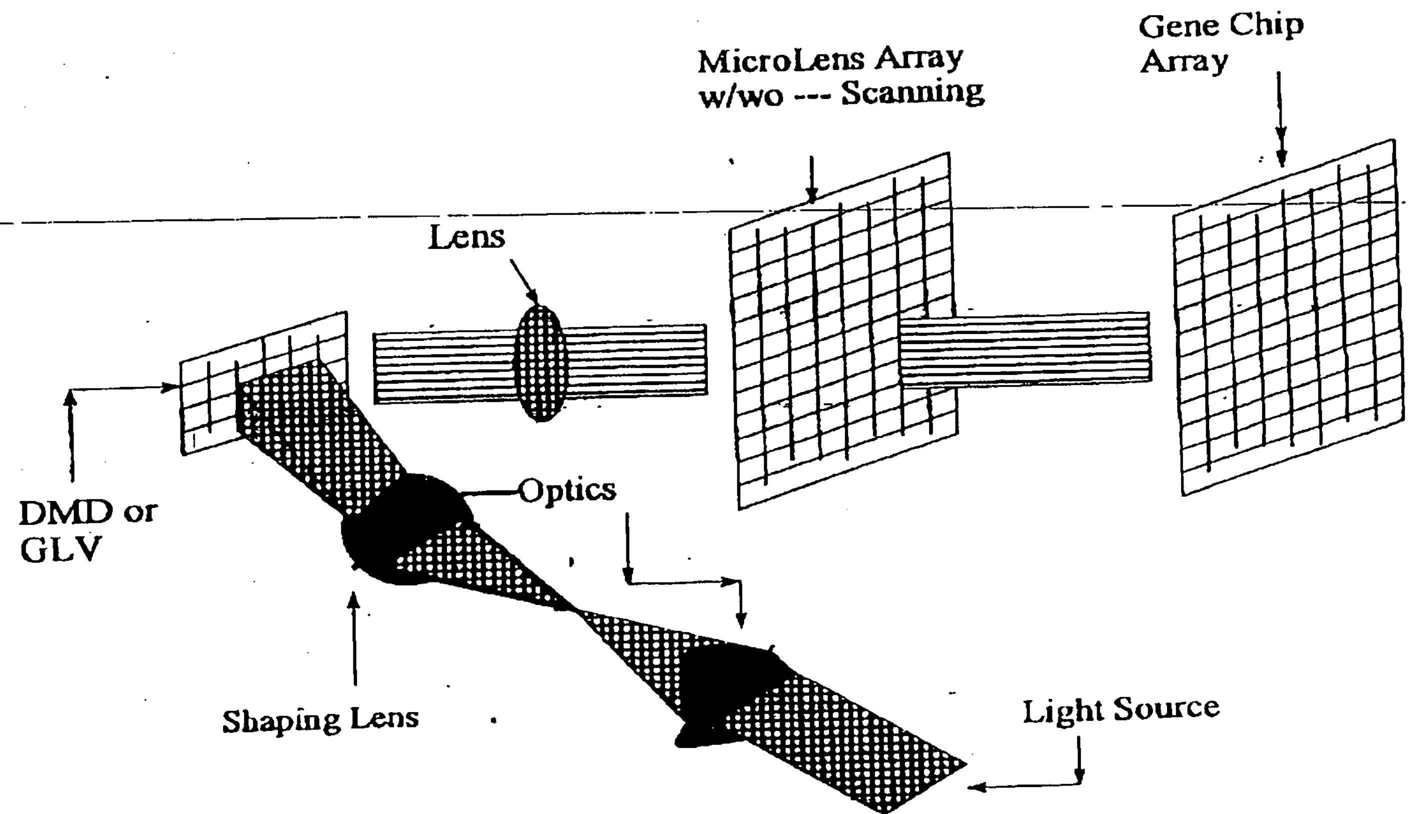

CHIP OR WAFER MOUNTED ON FLOW CELL (ON MULTIAXIS TRANSLATION/ROTATION STAGE IF NECESSARY)
REFLECTED LIGHT FROM MIRRORS THAT ARE ON IS IMAGED ONTO CHIP OR WAFER
ARC LAMP LIGHT (COLLIMATED, FILTERED, AND HOMOGENIZED)
REFLECTED LIGHT FROM MIRRORS THAT ARE OFF
LENS
NOT TO SCALE
MICRO-MIRROR ARRAY
THESE MIRRORS ARE OFF
THESE MIRRORS ARE ON

FIGURE 1

FIGURE 2



DIRECT WRITE LITHOGRAPHY with Mechanical Digital MicroMirrors

866250" EEEZ8009

50 μm 128·128 + 100 μm 64×64

FIGURE 3

2 Metal Zone Plates